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REDUCTIONS IN APROTIC MEDIA. I. CATHODIC REDUCTION LIMITS IN AC--ETC(U)

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by

B. Stanley Pons and S.B. Khoo

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Reductions in Aprotic Media. I. Cathodic Reduction Limits  
at a Platinum Electrode in Acetonitrile

Stanley Pons<sup>\*</sup> and S.B. Khoo

Department of Chemistry  
University of Alberta  
Edmonton, Alberta, Canada  
T6G 2G2

## ABSTRACT

The cathodic behavior of acetonitrile at a platinum electrode is strongly dependent on the cation of the supporting electrolyte, and contamination by moisture. Mixtures of supporting electrolytes can give anomolous effects under certain conditions; the results are consistent with the formation of hydride ion at the platinum surface.

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## INTRODUCTION

Fleischmann et al (1-3) have proposed the existence of hydride intermediates in the reduction of weakly acidic compounds at platinum and palladium electrodes in several solvent-electrolyte systems. In recent studies of the electrochemistry of lithium in aprotic systems, we have observed reactions that seem to be accounted for only by the presence of similar intermediates. In the present paper, we discuss the behavior of a platinum electrode in acetonitrile at cathodic potential with tetrabutylammonium tetrafluoroborate and lithium perchlorate electrolytes. Although these systems have been studied extensively (4) several reactions which we have observed have not been reported, and their presence seems critical in the overall description of the reduction mechanism at the cathodic limit. A knowledge of these reactions is paramount in the successful design of power device electrolytes using alkali metals. Subsequent papers (5,6) are concerned with other electrodes and solvent electrolytes, as well as further evidence of hydride formation and its effect on electrochemical studies of organic molecules.

We will point out that hydride production explains various anomalies in reduction of acetonitrile under certain conditions, specifically;

- (1) The difference in the effect of water on lithium solutions and tetraalkylammonium solutions,
- (2) the passivation of a platinum electrode in

tetraalkylammonium solutions in the presence of trace lithium, and

- (3) the difference in cathodic limits between tetraalkylammonium and lithium solutions.

## EXPERIMENTAL

Procedure for Controlled Potential Electrolysis

The electrolyses were performed in a glass H-cell. The anode and cathode chambers (70 ml capacity each) were separated by a third "buffer" chamber formed by inserting two medium porosity glass frits in the connecting tube between the two compartments. The electrodes were 16 ga platinum wire formed in coils and had an apparent surface area of  $8.0 \text{ cm}^2$ . The working electrode potential was probed with the use of a Luggin capillary placed in the chamber perpendicular to the electrode coil axis. The Luggin access was by a 7/25 glass joint. The electrodes were fused into glass and were mounted in the cell by 29/52 glass joints. Stirring was accomplished either by a glass encapsulated magnet or by argon gas purging of the solution. The potentials were controlled with respect to an  $\text{Ag}/\text{Ag}^+$  reference electrode which contained 0.1 M tetrabutylammonium tetrafluoroborate (or 0.1 M lithium perchlorate depending on the main cell electrolyte). The reference was isolated by a fine porous glass frit from the Luggin section. The electrolyses were run in constant potential mode.

After electrolysis, the catholyte was removed and diluted with 2 ml of distilled water, and the mixture evaporated to dryness on a rotary evaporator. The electrolyte salt was removed by taking up the residue in 50 ml of diethyl ether, and extracting with three 40 ml portions of saturated sodium chloride solution. The ether layer was isolated and dried over sodium



sulfate and evaporated to dryness on the rotary evaporator. The resulting residue was either vacuum sublimed, or chromatographed as described below.

#### Mass Spectroscopy

Mass spectra were taken of both the gas head above the catholyte solution, and of the catholyte itself. Samples were withdrawn through specially designed access ports fitted with silicone septums. Background samples were made from aliquots of original solution stored in a spare cell, and were subtracted from the sample spectra. All spectra were obtained on an AEI MS-50 mass spectrometer. The ionization energy was 70 e.v.

#### Instrumentation

Electrochemical experiments were performed with a Hi Tek Instruments DT2101 potentiostat, AA1 512 bit signal averager, PPR1 waveform generator, and output was to a Hewlett Packard 7345 x-y recorder.

#### Solvent Preparation

Acetonitrile (Caledon HPLC grade, nominal water content 0.003%) was refluxed under argon while over calcium hydride and Woelm neutral alumina (Super Grade 1), distilled from the mixture, and stored under argon over alumina.

#### Reaction of Isobutyraldehyde with the Acetonitrile Anion

Isobutyraldehyde (100 mg) was added to the catholyte

compartment containing 70 ml of 0.1 M TBAF in dry acetonitrile after electrolysis for 4 hours at -3.30 volts. The residue obtained after workup as described was chromatographed on XAD polystyrene resin (methyl alcohol:chloroform 1:100 to 100:1) yielding 51 mg of 3-hydroxy-4-methylvaleronitrile:  $M^+$  m/e 114,  $^1H$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  = 1.00 (d, 6H,  $CH_3$ ), 1.78 (m, 1H, CH), 2.69 (d, 2H,  $CH_2$ ), 3.28 (s, 1H, OH), 3.72 (q, 1H, CH); analysis  $C_6H_{11}NO$ .

#### Infrared Spectra

Consistently reproducible specular reflectance infrared spectra could be made of the surface of a 7 mm diameter platinum mirror electrode. After electrolysis at the potentials indicated in the text, the electrode was withdrawn carefully from the electrolysis cell under argon, washed with acetonitrile that had been purged with argon, and subsequently dried in an argon stream. The electrode was then placed into a reflectance attachment in the purged sample chamber of a Nicolet 7199 FTIR system. Spectra were obtained by ratioing 1000 single beam spectra of the electrode against the reference throughput of the spectrometer. From the result was subtracted 1000 spectra of a freshly polished electrode surface post-treated in the same way.

#### Kinetic Procedures

Using a surface coverage charge of  $208 \mu C cm^{-2}$  for smooth platinum, the calculated active area of a platinum wire cathode was calculated to be  $0.390 cm^2$ , giving a roughness factor of 4 to

the apparent area of  $0.098 \text{ cm}^2$ . The figure was obtained by averaging values obtained after cycles of measurement of the charge of desorption of hydrogen from  $1.0 \text{ M H}_2\text{SO}_4$  solutions in triply distilled  $\text{H}_2\text{O}$  with subsequent flaming of the electrodes for 10 seconds and cooling in an argon atmosphere. The relative standard deviation for the area determined in this manner was 4 ppt for 20 determinations. Solutions were degassed with dry argon, and measurements were made under an argon atmosphere.

Measurements were made in a 4.0 ml kinetic cell fitted with a Luggin capillary. Water was added to the cell with a 10  $\mu\text{l}$  syringe calibrated to 0.25% accuracy. All measurements were made at  $23.5^\circ\text{C}$ . For concentration values, temperature corrections were made to apparent volumes. The cell contained 3.60 ml of acetonitrile initially in the working compartment. Immediately before measurement, the solution was dried over calcium hydride pellets and Woelm neutral alumina (Super Grade I). The cell had been dried in vacuo in an oven at  $140^\circ\text{C}$  for 48 hours, cooled, and the oven subsequently brought to atmospheric pressure by admitting argon. If the background current at  $-3.20 \text{ V}$  was greater than  $15 \mu\text{A}$ , the procedure was repeated. This value insured a background current of less than 1% relative to that observed when the first 10  $\mu\text{l}$  sample of  $\text{H}_2\text{O}$  was added.

#### Electrolysis of Dry Acetonitrile Containing Tetrabutylammonium Tetrafluoroborate

Electrolysis at  $-3.30 \text{ volts}$  as described above of a  $0.1 \text{ M}$

tetrabutylammonium tetrafluoroborate solution for one hour and subsequent sublimation ( $40^{\circ}\text{C}$ ,  $10^{-2}$  torr) of the residue (after Fritz (4b)) followed by 2 recrystallizations from petroleum ether led to the isolation of the tautomeric 3-aminocrotonitrile/3-iminobutyronitrile mixture (60 mg):  $\text{M}^+$  m/e 82  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$  (3-aminocrotonitrile))  $\delta$  = 1.80 (s, 3H,  $\text{CH}_3$ ), 3.60 (M, 1H, CH), 4.71 (b, 2H,  $\text{NH}_2$ ), (100 MHz,  $\text{d}_6$ -acetone (3-iminobutyronitrile))  $\delta$  1.90 (s, 3H,  $\text{CH}_3$ ), 4.12 (s, 2H,  $\text{CH}_2$ ), 5.81 (b, 1H, NH), analysis  $\text{C}_4\text{H}_6\text{N}_2$ . Electrolysis under the same conditions for 6 hours yielded 180 mg of the tautomeric mixture when half of the product was worked up as described above. If the sublimation temperature was raised, additional product was isolated, which, after recrystallization from ethyl acetate yielded 85 mg of 4-amino-2,6-dimethylpyrimidine:  $\text{M}^+$  m/e 123,  $^1\text{H}$  NMR (100 MHz,  $\text{d}_6$ -acetone)  $\delta$  = 2.10 (s, 3H,  $\text{CH}_3$ ), 2.20 (s, 3H,  $\text{CH}_3$ ), 6.15 (s, 1H, ring H), 6.00 (b, 2H,  $\text{NH}_2$ ), analysis  $\text{C}_6\text{H}_9\text{N}_3$ . Extraction of the sublimation residue three times with 15 ml portions of ethyl acetate, followed by evaporation of the solvent and recrystallization leads to 2,4,6-trimethyl-1,3,5-triazine (22 mg):  $\text{M}^+$  m/e 123,  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.40 (s,  $\text{CH}_3$ ), analysis  $\text{C}_6\text{H}_9\text{N}_3$ .

#### Electrolysis of Dry Acetonitrile Containing Lithium Perchlorate

Electrolysis at -3.30 volts as described above of a 0.1 M solution of lithium perchlorate for 4.5 hours resulted in a mixture that was filtered before working up as described above. The filtrate yielded 175 mg of the tautomeric dimer mixture (see

previous paragraph) and 50 mg of 4-amino-2,6-dimethylpyrimidine (see previous paragraph). The white solid material collected from the filtration was washed with pure acetonitrile, and dried in a vacuum at 40°C. An atomic emission spectrum of a perchloric acid solution of 10 mg of the residue indicated the presence of lithium (6707.8 Å). Reactions of an aqueous solution of the residue toward copper ion, ammonia, and silver ion were positive for cyanide ion.

Electrolysis of Dry Acetonitrile Solution of Tetrabutylammonium Tetrafluoroborate Containing Lithium Ion

Electrolysis of a solution containing both electrolytes was carried out at -4.50 volts for 1 hour. After workup as described in the general procedure, chromatography was performed on the residue on XAD polystyrene resin (methyl alcohol:chloroform 1:50 to 50:1) yielding two reactions, one of which was sublimed as described above to yield 385 mg of the tautomeric dimer (see above) and 140 mg of the trimeric mixture (see above). The remaining fraction was tributylamine (139 mg): B.P. 209-210° (lit. 211° (13)) methyl iodide addition compound m.p. 184° (lit. 186° (13)), IR (NaCl plates, neat) 2945 (s), 2901 (s), 2825 (s), 1462 (s), 1379 (s), 1304 (m), 1185 (s), 1088 (s), 735 (b,m),  $M^+$  m/e 185, analysis  $C_{12}H_{27}N$ .

Electrolysis of Wet Acetonitrile Solutions Containing 0.1 M Tetrabutylammonium Tetrafluoroborate and/or Lithium Ion

Electrolysis at -2.20 volts for 3 hours of a solution that

was 0.1 M tetrabutylammonium tetrafluoroborate and 5% water and worked up as described in the general procedure yielded only acetamide from a chloroform extraction of the salt solution:  $M^+$  m/e 59, m.p. 82° (lit. 82.3° (14)),  $^1H$  NMR (100 MHz,  $CDCl_3$ ),  $\delta$  = 1.90 (s, 3H,  $CH_3$ ), 6.66 (b, 2H,  $NH_2$ ), analysis  $C_2H_5NO$ . At -2.70 volts for 3 hours, tributylamine was also obtained by the workup described in the previous paragraph. If lithium ion (0.1 M) was present in the 5% water - 0.1 M tetrabutylammonium tetrafluoroborate solution, the primary product at -2.20 volts was lithium hydroxide (by atomic absorption and its pH titration curve with dilute HCl solution). Tributylamine was isolated in small amounts (20 mg) at -2.70 volts for 3 hours. The head gas analyses are given in the results section.

## RESULTS

Rigorously dried acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate begins appreciable cathodic breakdown at a platinum electrode at -3.00 volts vs  $\text{Ag}/\text{Ag}^+$  reference (Figure 1). Dry acetonitrile containing 0.1 M lithium perchlorate behaves the same at -3.00 volts, but the increase of cathodic current is not so rapid as the solution of tetraalkylammonium salt (Figure 2). Electrodes held at hydrogen evolution potentials in sulfuric acid solution prior to use in the acetonitrile solutions displayed higher current slope activities. Addition of water to the cell after a 60 second potentiostatic electrolysis at -3.30 volts in each solution causes (a) no visible reaction in the tetraalkylammonium solution, and (b) evolution of hydrogen gas with precipitation of lithium hydroxide from the darkened platinum electrode in the lithium-containing solution.

Repetitive scan cyclic voltammetry (Figures 1 and 2) results in irreversible depression of the cathodic breakdown current for both anhydrous solutions; the effect being markedly more pronounced for the lithium-containing solution.

Potentiostatic electrolysis at -3.30 volts of the tetrabutylammonium tetrafluoroborate solution under anhydrous conditions results in the liberation of hydrogen gas. Addition of isobutyraldehyde after electrolysis as described by Becker and Fritz (4b) results in the isolation of 3-hydroxy-4-methylvaleronitrile. If a freshly electrolyzed solution was

worked up, 3-aminocrotonitrile and 3-iminobutyronitrile were isolated. At longer electrolysis times at -3.30 volts, 4-amino-2,6-dimethylpyrimidine and 2,4,6-trimethyl-1,3,5-triazine could also be isolated. If the electrolyte is replaced by lithium perchlorate, hydrogen evolution is not observed, but is replaced by methane gas evolution. Lithium cyanide is found after electrolysis as well as 3-aminocrotonitrile, 3-iminobutyronitrile, and 4-amino-2,6-dimethylpyrimidine. Saturation of this cell with deuterium gas during electrolysis has no effect on the product or product distribution but in the anhydrous tetrabutylammonium tetrafluoroborate solution, saturation with deuterium leads to the formation of hydrogen-deuterium (HD) gas during electrolysis.

Replacement of lithium electrolyte by sodium electrolyte results in the anodic displacement of the breakdown potential by approximately 300 mV. Methane gas is still evolved during potentiostatic electrolysis at -2.80 volts, and the same products are isolated (with sodium cyanide replacing lithium cyanide).

In anhydrous solution, the addition of trace lithium ion to 0.1 M tetrabutylammonium tetrafluoroborate solution results in the suppression of cathodic breakdown to potentials in excess of -4.00 volts vs  $\text{Ag}/\text{Ag}^+$  (0.01 M). Breakdown, when it occurs, does so very fast with respect to increasing negative potential. A mixture of hydrogen, methane, butene, acetonitrile oligomers, and tributylamine is formed.

Water was added to samples of anhydrous electrolyte. Voltammograms such as that in Figure (3) resulted for the



tetrabutylammonium tetrafluoroborate sample. Hydrogen and trace methane were evolved at all potentials greater than -1.90 volts, and acetamide was isolated after workup as described. Approximately 25% current yields of tributylamine and butene were formed at potentially greater than -2.70 volts.

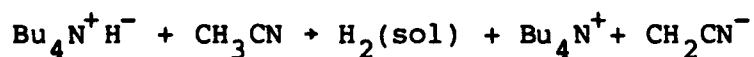
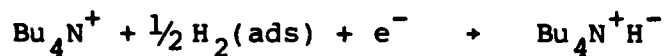
In solutions containing lithium with tetrabutylammonium tetrafluoroborate, hydrogen gas was evolved, and the other isolated products included lithium hydroxide (precipitated), and acetamide. No products due to acetonitrile reduction were observed, but tributylamine and butene were found in small amounts (<10% based on total coulombs passed) at electrolysis potentials of -2.70 volts or greater.

In wet lithium perchlorate solutions (Figure 7) the surface was also covered with lithium hydroxide (FTIR--see discussion), and only water reduction is observed (with rapid precipitation of lithium hydroxide and hydrogen evolution).

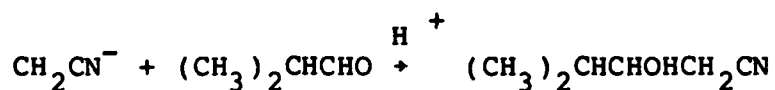
The FTIR reflectance infrared spectrum of the platinum surface after electrolysis of a 0.1 M lithium perchlorate solution at -1.90 volts for 60 seconds (Figure 4) was made, as well as a solution of 0.001 M lithium perchlorate and 0.1 M tetrabutylammonium tetrafluoroborate electrolyzed at -4.00 volts (Figure 5).

## DISCUSSION

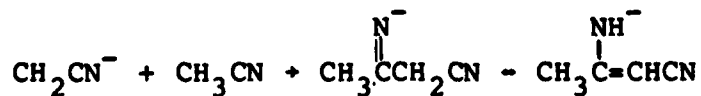
The electrochemical behavior of the anhydrous tetrabutylammonium tetrafluoroborate electrolyte system at a platinum electrode at -3.30 volts is consistent with the formation of an active hydride intermediate (1-2) that is soluble in the solvent system



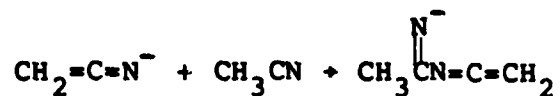
The carbanion is easily detected by its reaction with isobutyraldehyde to give 3-hydroxy-4-methylvaleronitrile .



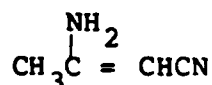
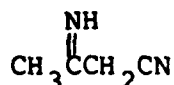
The anion is also known to react with acetonitrile to give the tautomeric mixture (4b)



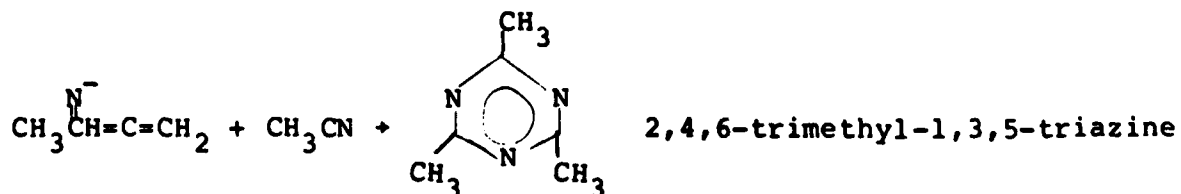
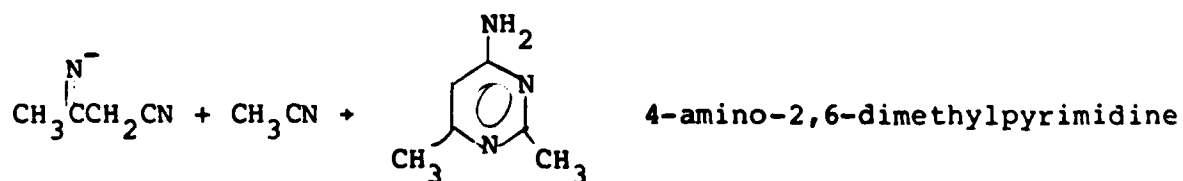
and, to a lesser degree,



The tautomers may react with a proton obtained from the solvent (or possibly electrolyte) to give the 3-iminobutyronitrile and the 3-aminocrotonitrile, both of which may be isolated:



Holding the electrolysis mixture at high negative potentials, (i.e. strongly basic conditions) for more extended periods of time leads to the formation of trimers by reaction of the dimer anions with acetonitrile:



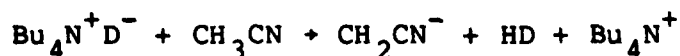
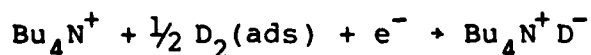
both of which were isolated. The hydride mechanism is supported by the increase of  $\text{CH}_4$  evolution when tetrabutylammonium

tetrafluoroborate is present. This indicates that  $\text{CH}_3\text{CN}$  reduction at the platinum surface, slow at this potential in the presence of lithium perchlorate, is increased due to the surface not being passivated by lithium hydride.

It has been suggested (1) that the initial reaction is due to preadsorbed hydrogen on the platinum surface. This is substantiated by the fact that cathodic preelectrolysis of the platinum surface in  $\text{H}_2\text{SO}_4$  solution leads to more rapid activation of the system. Also, saturation of the solution with  $\text{D}_2$  during electrolysis results in the formation of HD, again strongly supporting hydride formation mechanism at the platinum surface. Instead of the generated  $\text{H}_2$  being readsorbed, saturation of the solution with deuterium gas effects the surface exchange

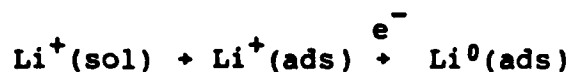


resulting in deuteride activation

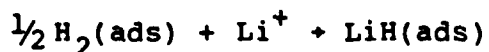


The HD was detected by mass spectroscopy.

In lithium perchlorate solutions with anhydrous acetonitrile, a different mechanism is in control. First, there is the underpotential deposition of lithium of about -1.00 volts

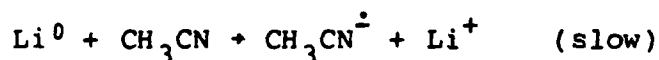


At -3.00 volts, any hydride that may be formed by preadsorbed hydrogen will be retained at the surface as the insoluble lithium hydride (3)

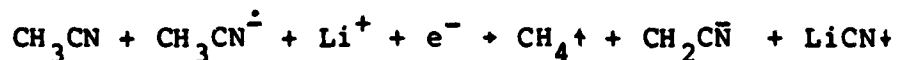
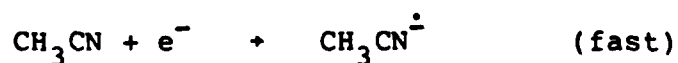


This insoluble surface compound is unreactive on short time scales toward acetonitrile, and further hydride formation does not occur at the new surface.

At higher cathodic potentials, however (-3.30 volts) direct electron transfer to the acetonitrile takes place (4b)



and/or

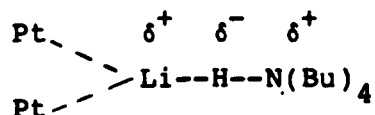


The anion then reacts as in the case of tetrabutylammonium tetrafluoroborate with more acetonitrile to give the dimeric and

trimeric products. Methane is found by mass spectroscopy, the salt is collected by filtration, and the acetonitrile dimers and trimers were analyzed as described.

In the presence of trace amounts of lithium ion, the tetrabutylammonium tetrafluoroborate solutions behave markedly different. The cathodic breakdown potential is now in the -4.50 volt range, and rapid formation of all of the acetonitrile/electrolyte reduction products is observed at these potentials.

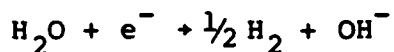
The infrared spectrum of a platinum electrode surface electrolyzed at -4.00 volts for 60 seconds in 0.001 M lithium perchlorate and 0.1 M tetrabutylammonium tetrafluoroborate indicates the presence of the tetrabutylammonium group bound to the surface. The surface is highly reactive toward water, releasing hydrogen gas if placed in a small cell of water fitted with a septum for sampling the gas. The resulting supernate contains lithium ion. The tetrabutylammonium group is not found in the infrared spectrum if the experiment is repeated without lithium ion being present. It is suspected that the surface hydride is partitioned between lithium and tetrafluoroborate resulting in strong adsorption of tetrabutylammonium and subsequent passivation of the electrode toward electron transfer to the solvent:



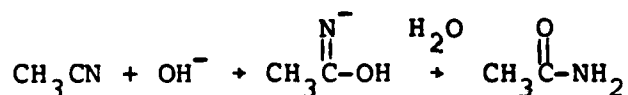
It should be pointed out that Fleischmann et al. have reported

passivation of the electrode by precipitated lithium hydride alone, but in their case the solvent (hexamethylphosphoramide) was not reactive toward the hydride.

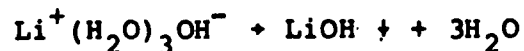
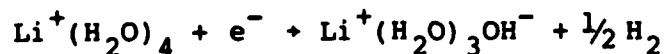
Addition of water to the tetrabutylammonium tetrafluoroborate system results in an anodic shift in the cathodic breakdown potential (Figure 3). Water is reduced to form hydroxide ion at -2.00 volts.



The high concentration of  $\text{OH}^-$  in the double layer effects hydrolyses of acetonitrile to acetamide (11):

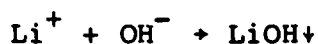
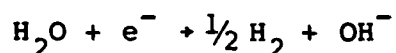


which is observed in the product analysis. The mechanism may be checked by providing a reagent that will rapidly remove hydroxide. Lithium ion was added to the solution. Water is known to complex strongly with lithium ion (7-9). The reduction peak at -1.9 volts (Figure 6) in the wet lithium solution seems to be the reduction of the acidic lithium tetraaquo complex



with the following cathodic limit (now shifted to -2.30 volts due

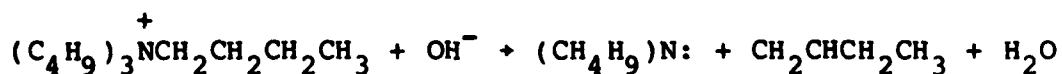
to passivation by lithium hydroxide) being breakdown of the bulk water and tetrabutylammonium ion. The LiOH on the electrode was determined by reflectance IR spectroscopy (Figure 4). At more negative potentials ( $>-2.20$  V), electrolysis of water is accompanied by the precipitation of LiOH



The percentage of acetamide was greatly reduced due to the loss of hydroxide ion to insoluble lithium hydroxide formation.

That the peak at  $-1.90$  volts is due to a hydrate species is further substantiated by the curve in Figure 8. The peak height increases linearly with water concentration approaching  $0.25$  M. The curve is subsequently pushed up due to the prewave of further reductions at potentials greater than  $-2.10$  volts.

Hydroxide ion in high concentrations apparently is responsible as well for the formation of butene and tributylamine present in the wet tetrabutylammonium tetrafluoroborate electrolysis mixture. This reaction is well known in reductive electrochemistry of arylhalides in acetonitrile (10).



In contrast, a wet solution of lithium perchlorate (Figure 7) exhibits only water breakdown after the peak at  $-1.90$  volts;



the tetrabutylammonium reduction is absent.

We have preliminary evidence that the presence of hydride in lithium battery environments severely alters solvent interaction near the surface. For instance, new infrared bands that appear due to molecular complex formation in lithium bromide/acetonitrile/sulfur dioxide electrolyte mixtures are destroyed as lithium hydride is formed at a platinum cathode. Unstable hydride compositions and ion-solvent interactions in these systems are being studied with in situ EMIRS (15-17) techniques.

## ACKNOWLEDGEMENT

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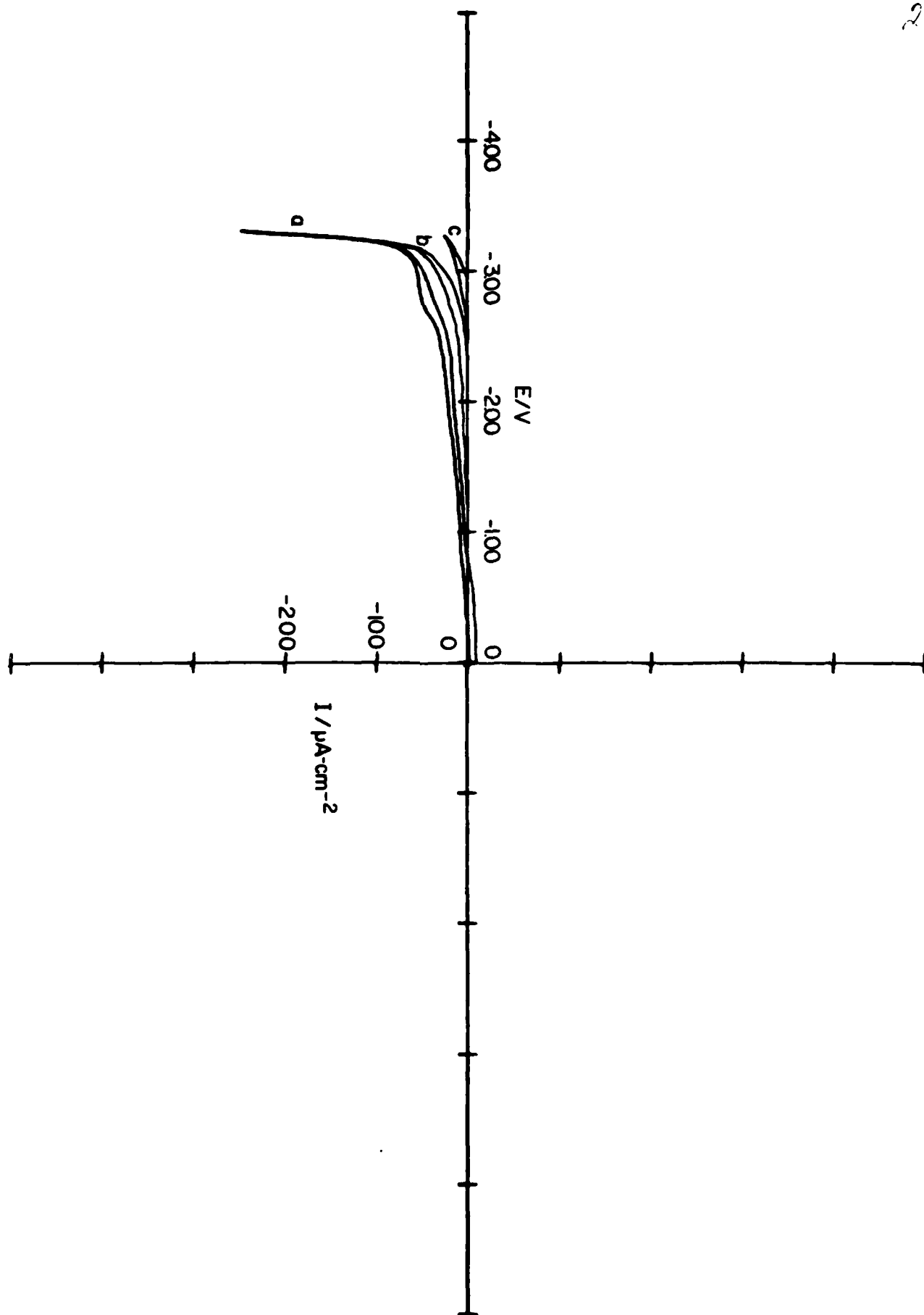
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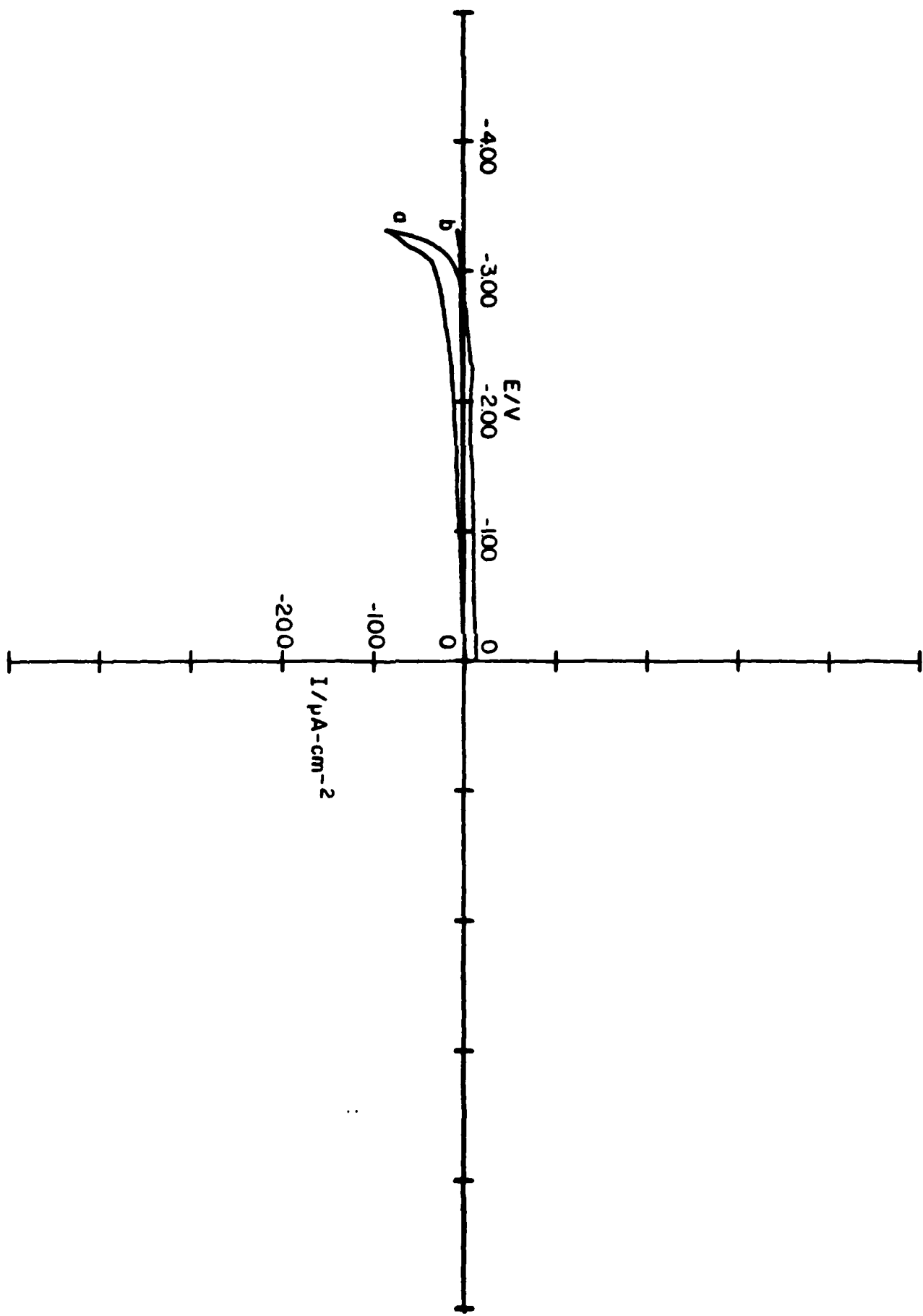
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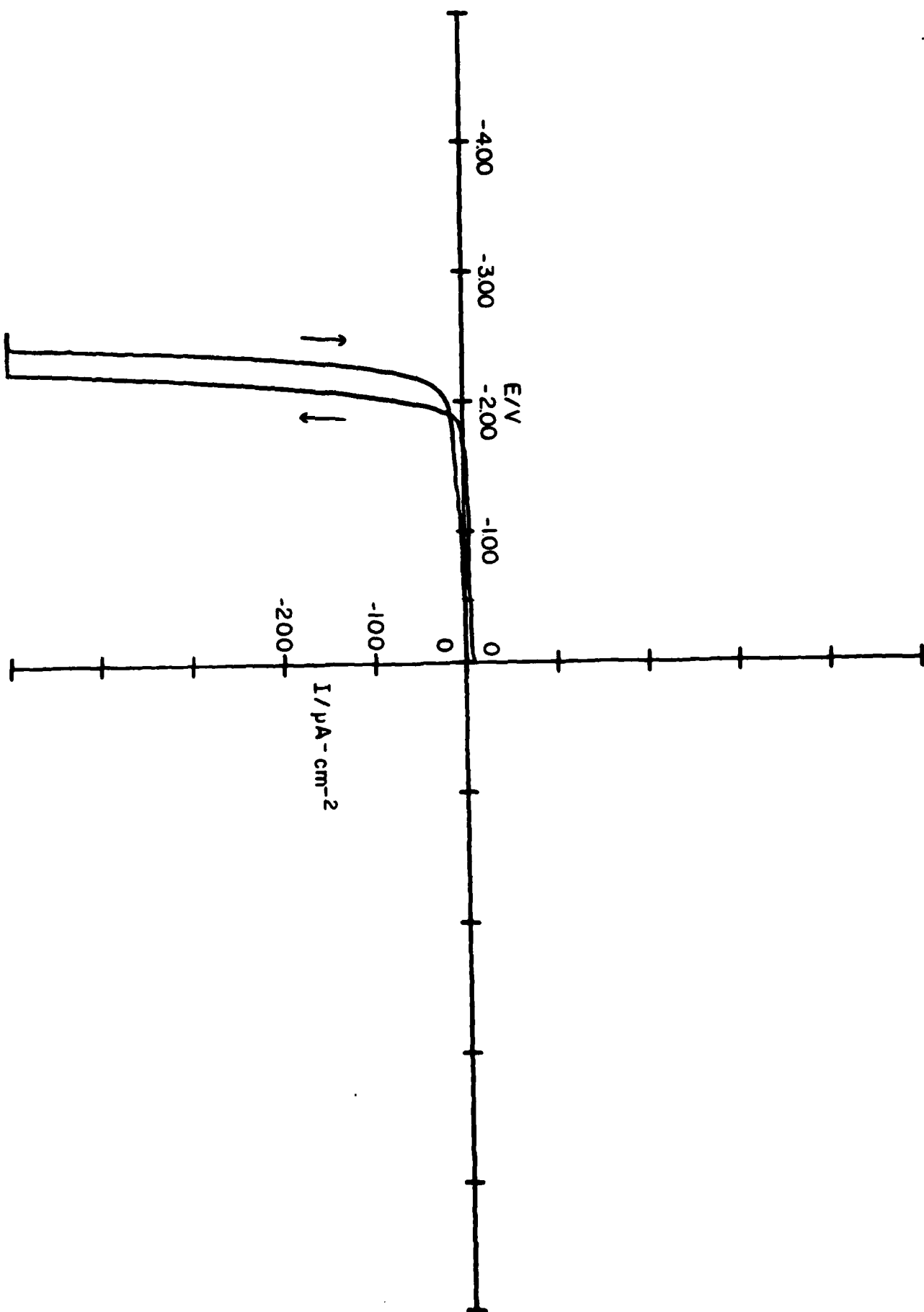
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## FIGURE LEGENDS

- (1) Cyclic voltammogram of 0.1 M tetrabutylammonium tetrafluoroborate in anhydrous acetonitrile. Sweep rate -  $100 \text{ mV-s}^{-1}$ , E vs.  $\text{Ag/Ag}^+$  (0.01 M) reference. (a) 1st sweep, (b) 2nd sweep, (c) 3rd sweep.
- (2) Cyclic voltammogram of 0.1 M lithium perchlorate in anhydrous acetonitrile. Other parameters same as Figure 1.
- (3) Cyclic voltammogram of 0.1 M tetrabutylammonium tetrafluoroborate and 1.7% water in acetonitrile. Other parameters same as Figure 1.
- (4a) Reflectance infrared spectrum of Pt electrode electrolyzed in wet 0.1 M lithium perchlorate for 60 seconds at -1.90 V.  
( b) Literature (13) spectrum for lithium hydroxide.
- (5a) Reflectance infrared spectrum of Pt electrode electrolyzed in dry 0.1 M tetrafluoroborate and 0.001 M lithium perchlorate for 60 seconds at -4.00 V.  
( b) Standard tetrabutylammonium tetrafluoroborate transmission.
- (6) Cyclic voltammetry of 0.01 M lithium perchlorate, 1.7% water, and 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile. Other parameters same as Figure 1.
- (7) Cyclic voltammetry of 0.1 M lithium perchlorate and 1.7% water in acetonitrile. Other parameters same as Figure 1.
- (8) Plot of steady state current density vs. water concentration for electrolysis of a 0.1 M lithium perchlorate solution at -1.90 volts.



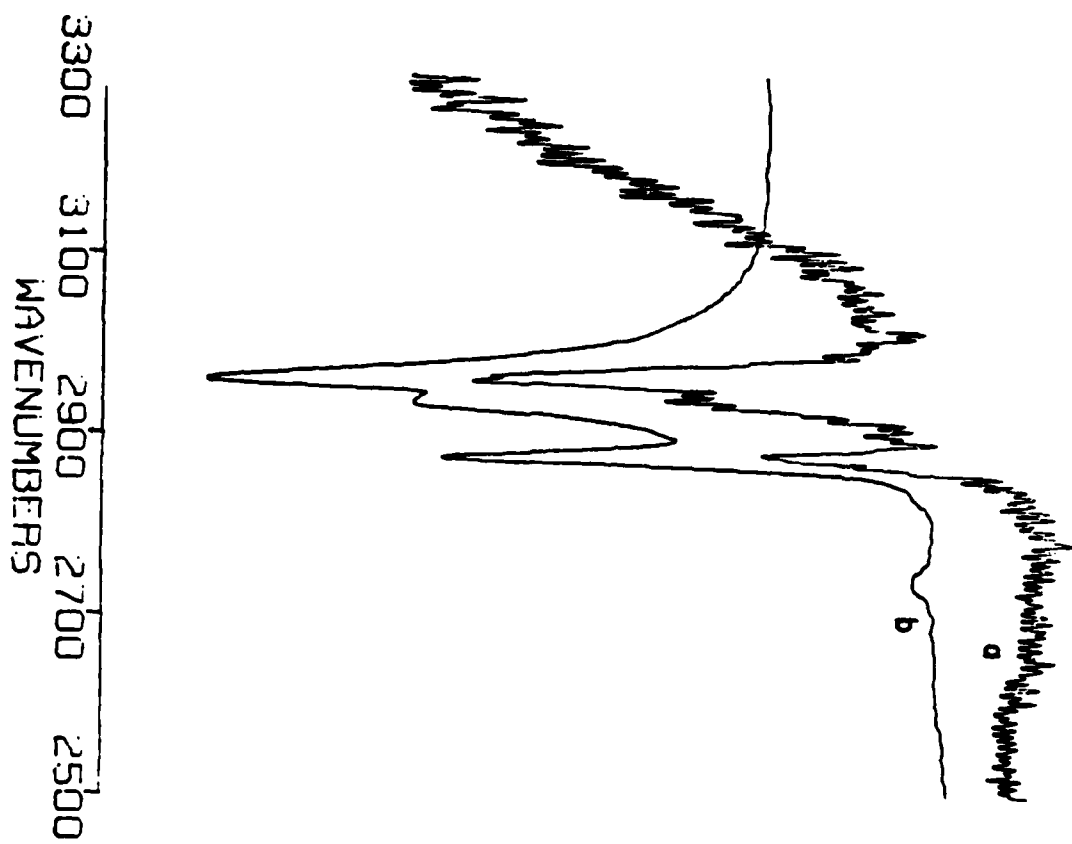


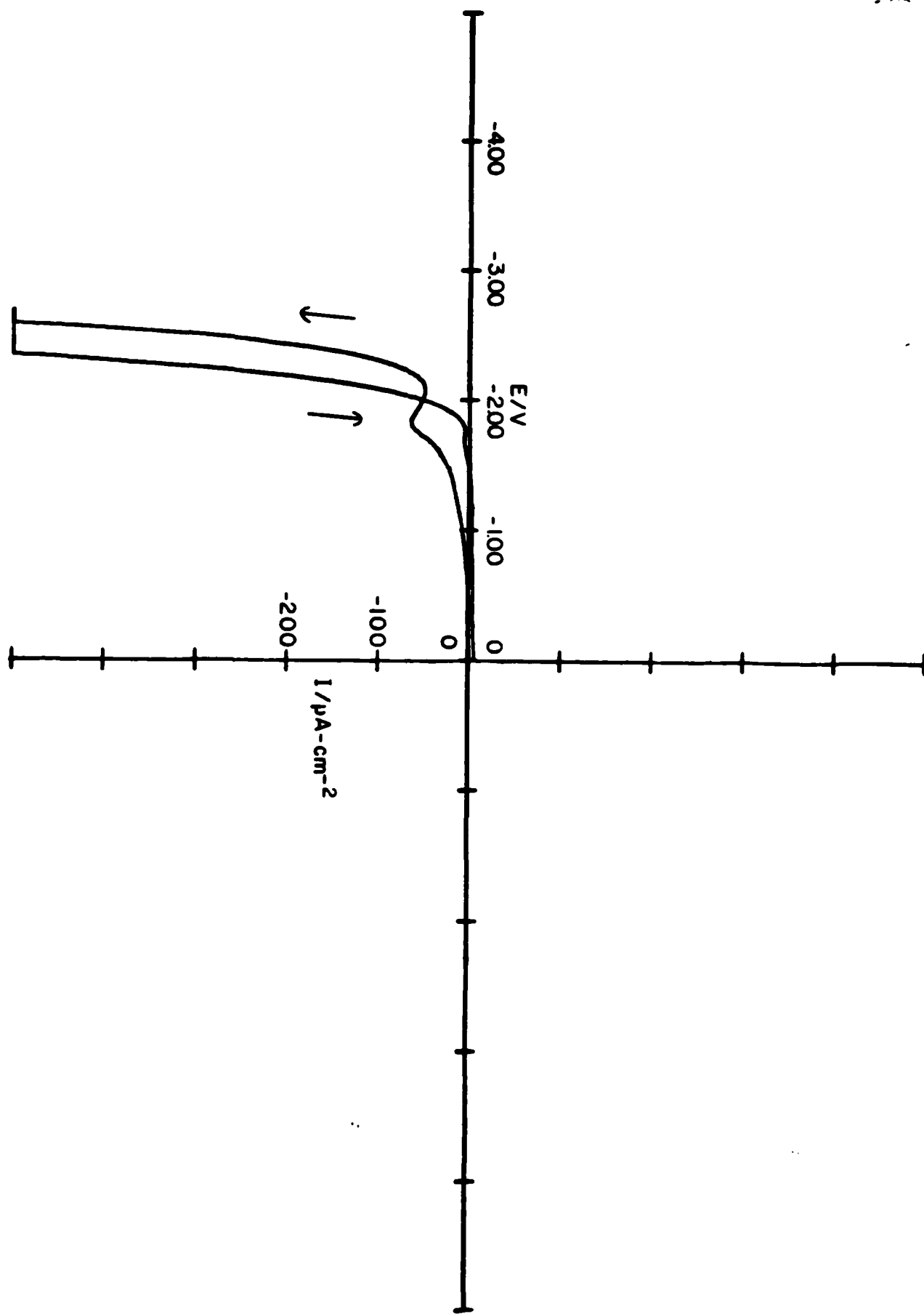


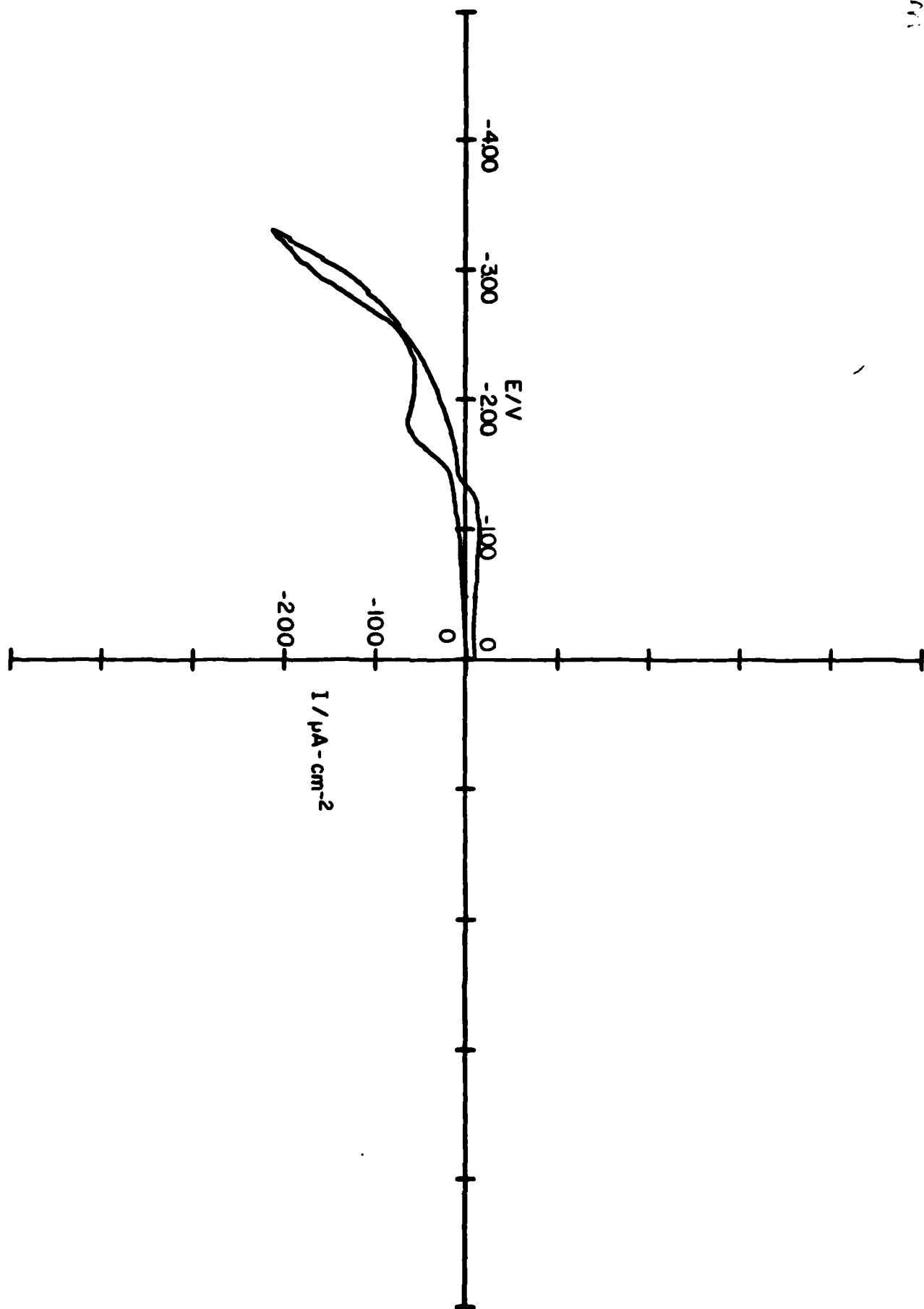


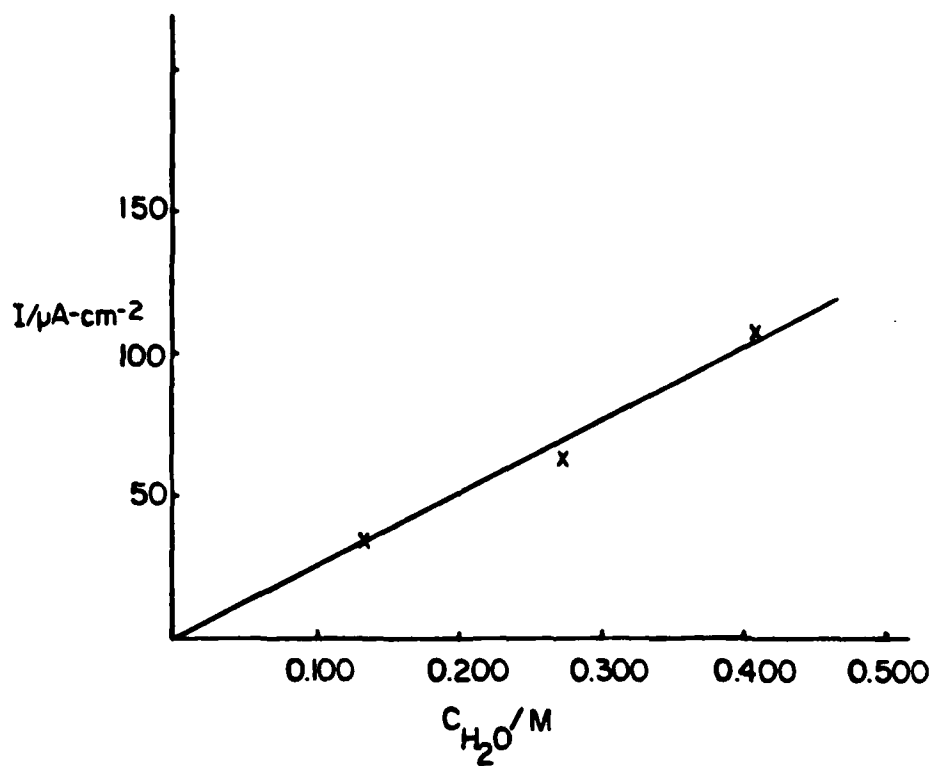
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